SOLVATING COMPONENT AND SOLVENT SYSTEM FOR MESOPHASE PITCH

CROSS-REFERENCE OF RELATED APPLICATIONS

[0001] This application is a division of application No. 09/873,754 filed on June 4, 2001, which is incorporated herein by reference. This application claims priority to U.S. Provisional Application No. 60/211,439, filed June 13, 2000.

BACKGROUND OF THE INVENTION

Field of the Invention

[0002] The present invention relates to improvements in solvated mesophase pitch. More specifically, the current invention provides a solvent system suitable for use as the solvating component of high melting or unmeltable mesophase pitches. Additionally, the current invention provides a solvent system suitable for producing a high molecular weight mesophase pitch.

Prior Art

[0003] Mesophase pitches are carbonaceous materials which contain mesophases exhibiting optical anisotropy due to an agglomerated layered structure. The molecules have aromatic structures which through interaction are associated together to form ordered liquid crystals which are either liquid or solid depending on temperature. Mesophase pitch is not ordinarily available in existing hydrocarbon fractions obtained from normal refining procedures. Mesophase pitch, however, can be prepared by treatment of aromatic feedstocks which is well known in the art. In known processes, a growth reaction converts relatively small aromatic molecules into larger mesophase-size molecules and these molecules are concentrated. Thus, mesophase is extracted from pitch by treatment of aromatic feedstocks.

[0004] It is known that mesophase pitches can be drawn into pitch based carbon fibers which have numerous commercial uses. A challenge in preparing a high-performance carbon fiber from a mesophase pitch resides in the fact that a significantly high temperature is necessary to use at the spinning stage because of the high softening point of the pitch.

[0005] The present invention is a product of ongoing research in the field of solvated mesophase pitch. Solvated mesophase pitches were disclosed as early as U.S. Patent No. 5,259,947 (owned by the Assignee herein) which is incorporated herein by reference. The

solvated mesophase contains a small percentage by weight of solvent in the liquid crystalline structure so that it melts or fuses at a lower temperature. As noted, in the '947 Patent and subsequent patents relating to this subject matter, solvated mesophase pitch has several advantages over traditional mesophase pitch. A primary advantage is the ability to use high melting or unmeltable mesophase pitch in carbon fiber spinning processes.

[0006] Prior to the current invention, the principal solvents used as the solvating component consisted of 1 to 3 ring aromatic compounds. The aromatics are a series of hydrocarbon ring compounds. While these 1 to 3 ring compounds are effective, they provide only a limited range of compatibility with heavy aromatic pitches.

[0007] In some applications, it is advantageous to have higher boiling point solvating solvents. This allows processing of the melted pitches at ordinary (in other words, atmospheric) pressure.

[0008] It is additionally advantageous to have higher boiling point solvating solvents which extend to higher temperatures. This will extend the range over which solvent evaporation rates are controlled when making or processing pitch artifacts.

[0009] It is, therefore, a principal object and purpose of the present invention to produce new solvents which makes processing of the carbon pitches more facile.

[0010] It is a further additional object and purpose of the present invention to produce a new solvent or solvating agent which solvates especially high melting mesogens.

[0011] It is a further object and purpose of the present invention to produce a novel solvent which promotes increased fiber attenuation during spinning.

[0012] It is a further object and purpose of the present invention to provide a high boiling point aromatic solvent as a useful component in extracting solvents in order to isolate heavy aromatic pitches from isotropic or mesophase pitches.

[0013] It is a further object and purpose of the present invention to isolate mesogenic insolubles by solvent fractionation.

SUMMARY OF THE INVENTION

[0014] The current invention provides a solvent system suitable for use as the solvating component of a solvated mesophase pitch. The solvent system comprises a mixture of aromatic hydrocarbons having boiling points in the atmospheric equivalent boiling point ("AEBP") range of about 285° to about 500°C (about 550° - 932°F). In the solvent system, at least 80% of the carbon atoms are aromatic as characterized by carbon 13 NMR.

[0015] The aromatic hydrocarbon compounds making up the solvent system are selected

from the group consisting of (i) aromatic compounds and N, O and S heteroaromatic compounds having 2 to 5 aromatic rings, (ii) substituted aromatic compounds and N, O and S heteroaromatic compounds having 2 to 5 aromatic rings wherein said substituents are alkyl groups having 1 to 3 carbons (C_1 to C_3), (iii) hydroaromatic compounds and N, O and S heteroaromatic compounds having 2 to 5 aromatic rings, (iv) substituted hydroaromatic compounds and N, O and S heteroaromatic compounds having 2 to 5 rings wherein said substituents are alkyl groups having 1 to 3 carbons, and (v) mixtures thereof. Additionally the aromatic hydrocarbon compounds can contain up to ten weight percent (10%) heteroatoms of nitrogen, oxygen and sulfur. When present, the heteroatoms predominately occur in stable aromatic ring structures such as pyrroles, pyridines, furans and thiophenes. The new solvents proposed herein facilitate the handling and use of solvated mesophase pitch.

[0016] The current invention additionally provides a solvent system for extracting isotropic and mesophase pitches. The solvent system suitable for extracting the pitches comprises a first solvent system as described above for solvating a mesophase pitch in combination with a second aromatic solvent system comprising 1 to 3 ring aromatic compounds having a solubility parameter in the range of 8 to 11.5 wherein said substituents are alkyl groups having 1 to 3 carbons, and mixtures thereof. The ratio of the first solvent system to the second solvent system may range from about 1:20 to about 2:5.

[0017] The extraction solution is added to a pitch in a solution to pitch ratio ranging from about 3:1 to about 20:1. The pitch is then extracted to yield a mesogen residue. Using the inventive solvent system, one achieves excellent control of the extraction process. Additionally, any residual solvent in the mesogen product is a suitable solvent for forming a solvated mesophase pitch.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] Figures 1 through 5 illustrate examples of aromatic compounds that make up the solvent system which comprise a part of the present invention;

[0019] Figure 6 is a diagrammatic representation of an extraction process to produce a high molecular weight mesophase pitch in accordance with the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0020] The embodiments discussed herein are merely illustrative of specific manners in which to make and use the invention and are not to be interpreted as limiting the scope of the instant invention.

[0021] While the invention has been described with a certain degree of particularity, it is to be noted that many modifications may be made in the details of the invention's construction and the arrangement of its components without departing from the spirit and scope of this disclosure, it is understood that the invention is not limited to the embodiments set forth herein for purposes of exemplification.

[0022] The present invention provides a solvent system for use as the solvating component of a solvated mesophase pitch. The current invention also provides a solvent system for extracting isotropic and mesophase pitches. The present invention allows isolation of mesogenic insolubles by solvent fractionation. Additionally, the present invention provides a high molecular weight mesophase pitch and a process to produce a high molecular weight mesophase pitch.

[0023] The solvents of the invention are versatile, but inexpensive, that can be used to facilitate the processing of isotropic and mesophase pitches. The hydrocarbons in the preferred embodiment have at least 80% of the carbon atoms as aromatic. The aromatic content may be determined by carbon 13 NMR (a naturally occurring isotope testing). The solvents can be employed both as solvents and co-solvents to aid in the extraction of isotropic and mesophase pitches and as solvating agents to lower the viscosity of pitches. Whether they act as extraction solvents or solvating agents depends upon the amount of solvent combined with the pitch and/or whether a co-solvent is used.

[0024] As extraction solvents, the aromatic solvents of the invention are generally combined with lower solubility parameter neat aromatic hydrocarbon solvents, such as toluene, xylene, or benzene, to produce mixed solvents systems. The mixed solvents are used to extract isotropic and mesophase pitches in solvent-to-pitch ratios of 3:1 to 20:1. Thermally cracked solvents in the mixed solvent increase solvent solubility parameters, and thereby promote extraction of high molecular weight material from isotropic and mesophase pitches which results in heavy or high molecular weight, high melting mesogens as the extraction residue. The yield of mesophase is indirectly related to the concentration of aromatic solvent of the invention in the mixed solvents; the melting point of the mesogens is directly related to solvent concentration; consequently, concentration of aromatic solvent used in extractions of isotropic and mesophase pitches is useful in controlling properties of the resulting residual mesogens.

[0025] Aromatic solvents of the invention can also be used to solvate mesogens. At low solvent amounts of 5 to 30 weight percent, the resulting solvated mesophase pitch is typically 100 percent anisotropic. At higher solvent amounts of 20 to 40 or more weight percent

solvent, there tends to be up to 60 volume percent isotropic phase in the solvated mesophase pitch. The fluid or melting temperature of the solvated mesophase pitch generally decreases with increasing solvent addition. In many uses the most desirable solvated mesophase pitch is the pitch having the lowest melting or fluid temperature consistent with maintaining 100 percent anisotropy. Since higher solvent contents give lower fluid temperatures, this corresponds to the highest solvent content solvated mesophase pitch consistent with maintaining 100 percent anisotropy. It has been discovered that this most desirable product is obtained with highly aromatic mixed solvents. Substantially aromatic mixtures having >80% and preferably >85% aromatic carbons by carbon 13 NMR testing are effective.

[0026] It has further been discovered that a fairly narrow boiling range aromatic solvent is preferred. The preferred aromatic solvent has at least 80 percent of its components boiling within ±60°C and more preferably within ±30°C of the mean boiling point.

[0027] The ability to reduce the viscosity of solvated mesophase pitches and to control the melting temperature of mesogens by the addition of aromatic solvents is useful in mesophase pitch applications such as pitch carbon fiber spinning and composite impregnation. In particular with regards to fiber spinning, mesophases solvated with these solvents can be spun at lower temperatures. In addition, there is better control of attenuation during spinning using the solvents of the present invention. Evaporation of volatile pitch components from the hot molten pitch at the die tip is one of the factors limiting the ability to attenuate pitch fibers to small diameters. Aromatic solvents of the invention can have very low vapor pressures at the solvated pitch spinning temperatures, thereby allowing excellent pitch attenuation to small diameter fibers.

[0028] The aromatic solvents of the present invention are mixtures of aromatic hydrocarbons having boiling points in the atmospheric equivalent boiling point range of about 285° to about 500°C (about 550°-932°F). At least 80% of the carbon atoms of the hydrocarbons are aromatic as measured by carbon 13 NMR. The aromatic hydrocarbons are selected from the group consisting of (i) aromatic compounds and N, O and S heteroaromatic compounds having 2 to 5 rings, (ii) substituted aromatic compounds and N, O and S heteroaromatic compounds having 2 to 5 rings wherein substituents are alkyl groups having 1 to 3 carbons, (iii) hydroaromatic compounds and N, O and S heteroaromatic compounds having 2 to 5 rings, (iv) substituted hydroaromatic compounds and N, O and S heteroaromatic compounds having 2 to 5 rings wherein said substituents are alkyl groups having 1 to 3 carbons and (v) mixtures thereof. Additionally the aromatic hydrocarbon compounds can contain up to ten weight percent heteroatoms of nitrogen, oxygen and sulfur. When present,

the heteroatoms predominately occur in stable aromatic ring structures such as pyrroles, pyridines, furans and thiophenes.

[0029] Figures 1 through 5 illustrate non-limiting examples of aromatic hydrocarbons useful in the present invention. Figure 1 illustrates an example of an aromatic compound having 2 to 5 rings, in this case, a four ring aromatic, chrysene. Figure 2 illustrates an example of a substituted aromatic compound having 2 to 5 rings wherein the substituents are alkyl groups having 1 to 3 carbons. In this case, a four ring alkyl aromatic, 1,7-dimethylchrysene. Figure 3 illustrates an example of a hydroaromatic compound having 2 to 5 rings, in this case a four ring hydroaromatic, 5,6-dihydrochrysene. Figure 4 illustrates an example of a substituted hydroaromatic compound having 2 to 5 rings wherein the substituents are alkyl groups having 1 to 3 carbons, in this case, 1-methyl, 5,6-dihydrochrysene. Finally, Figure 5 illustrates a sulfur-containing heterocyclic aromatic compound having 2 to 5 rings with a thiophenic ring, dibenzothiophene.

[0030] Aromatic solvents suitable for the present invention can be obtained from a number of sources including refinery coker liquids, gas oils, decant oils, coal tars and chemical tars such as ethylene tars. Such naturally occurring mixtures are preferred over pure compounds in the inventive range because they are readily available, much lower in cost and tend to remain liquid over a wide range of useful temperatures. In some cases the solvent must be thermally cracked to increase aromatic carbon content to greater than 80% in order to make the solvent useful.

[0031] In a preferred embodiment of the invention, the aromatic solvent is obtained from thermally cracked decant oil distillate. Decant oil is topped to prepare a distillate boiling in the range of 285° to 500°C. This clean distillate is thermally cracked at 400° to 540°C at up to 1000 psig for a time sufficient to convert the residue to greater than 80% and preferably greater than 85% aromatic carbons as measured by carbon 13 NMR. The thermally cracked decant oil distillate is vacuum distilled to obtain an aromatic solvent having the boiling range, aromaticity and chemical structures described herein for the inventive solvent.

[0032] A process of using the aromatic solvents of the present invention to produce high molecular weight mesogens is illustrated in Figure 6. Initially, the first aromatic solvent having boiling points in the atmospheric equivalent boiling point range of about 285° to 500°C are combined with a second solvent system. The first aromatic solvent is the heavy aromatic solvent of the invention described above. The second solvent system has a solubility parameter in the range of 8 to 11.5. The ratio of the first solvent system to the second solvent system ranges from 1:20 to 2:5. The combination of the first aromatic solvent and the second

aromatic solvent results in an extraction solution. The extraction solution is thereafter added to a pitch, in a solution to pitch ratio ranging from about 3:1 to about 20:1. Thereafter, the pitch is extracted by use of the extraction solution. The yield is a residue of mesogens.

[0033] The addition of the inventive aromatic solvent to a secondary solvent increases the solubility parameter of the extraction solution. The higher solubility parameter promotes extraction, resulting in recovery of high molecular weight, high melting mesogens. Mesogens melting at a temperature of 375°C or above are easily obtained.

Example 1.

[0034] Example 1 shows saturation data for the stepwise addition of an aromatic solvent of the invention to dry mesogens. Mesogens for Example 1 were obtained by extracting a mesogen-containing isotropic pitch prepared from a thermally treated decant oil fraction. The mesogens in the Example melt at 475°C as measured by hot stage microscopy. The dry mesogens were combined with increasing amounts of aromatic solvent fractionated from thermally cracked decant oil distillate. Greater than 80% of the solvent boils between 393° and 421°C. Three and four ring aromatics and simple derivatives comprise a substantial portion of material in this boiling range by gas chromatography/mass spectroscopy (GCMS). The solvent tested 90.0% aromatic carbons by carbon 13 NMR.

[0035]

Mesogen Melting Point, °C		**Aromatic Solvating Solvent**		**Solvated Mesophase**	
		Boiling Range, °C	**Added Conc., %**	**% Anisotropy**	**T@1000 P&100s^{-1}, °C**
475	With	393-421	18.2	100	300
		393-421	20.2	100	297
		393-421	22.2	100	293
		393-421	24.2	100	282
		393-421	26.2	100	280
		393-421	28.2	100	266
		393-421	30.2	97	260
		393-421	32.2	90	253

Increasing amounts of solvent decreases the fluid temperature of the solvated mesophase. The fluid temperature is shown as the temperature at which the pitch exhibits a viscosity of ~1000 poise at a shear rate of ~100 reciprocal seconds. With this combination of mesogens and solvent, the mesogens become saturated with solvent at around 28 to 30 weight percent. Higher solvent content solvated mesophases are partly isotropic.

Example 2.

[0036] Example 2 shows the improved effectiveness of more aromatic solvents of the invention. Mesogens melting at 395°C and obtained by extraction of a mesogen-containing pitch are combined with 22% aromatic solvent, greater than 80% of which boils between 338° and 366°C. Two, three and four ring aromatics and simple derivatives comprise a substantial portion of the material in this boiling range according to GCMS analysis.

[0037] The aromatic solvents vary from 83 to 89% aromatic carbons by carbon 13 NMR. The more aromatic solvents give lower solvated mesophase fluid temperatures indicating better solvating effectiveness. All of the solvents combined with these mesogens form solvated mesophases with similar small amounts of isotropic phase. Combining 22% 393° to 421°C boiling solvent of increasing aromatic carbon contents to the mesogens of this Example shows the same trend of reduced fluid temperature for more aromatic solvent.

Mesogen Melting Point, °C		Aromatic Solvating Solvent			Solvated Mesophase	
		Boiling Range, °C	Aromatic Carbon, %	Added Conc, %	% Anisotropy	T@1000 P&100s^{-1}, °C
395	With	338-366	83	22	96	216
		338-366	87	22		215
		338-366	89	22	90	211
		338-366	88	22	96	209
395		393-421	85	22		231
		393-421	87	22		224
		393-421	91	22	90	226
		393-421	90	22	88	218

Example 3.

[0038] Example 3 is a comparison between an aromatic solvent of the invention and a less aromatic solvent, not of the invention. Mesogens melting at 404°C and obtained by extraction of a mesogen-containing pitch were combined with 19 to 28% of each solvent. One observes that the ~83% aromatic carbon solvent of the invention combines with the mesogens of this Example to produce a 100% anisotropic solvated mesophase with a fluid temperature <233°C. The lowest fluid temperature obtained at 100% anisotropy with the ~72% aromatic comparative solvent is about 260°C.

[0039] The aromatic solvent of the invention of Example 3 was analyzed as containing 1.1% sulfur by elemental analysis. Greater than 90% of this sulfur was found to be in

thiophenic aromatic structures.

Mesogen Melting Point, °C		Solvating Solvent Boiling Range, °C	Aromatic Carbon, %	Added Conc, %	Solvated Mesophase % Anisotropy	T@1000 P&100s^{-1}, °C
404	With	340-400	~83	19	100	248
		340-400	~83	22	100	242
		340-400	~83	25	100	233
		340-400	~83	28	96	226
		393-416	~72	19	100	257
		393-416	~72	22	99	262
		393-416	~72	25	93	257
		393-416	~72	28	87	255

Example 4.

[0040] Example 4 shows solvated mesophase pitches formed from mesogens and relatively high and low boiling aromatic solvents of the invention. This illustrates the breadth of applicability of the current teaching.

Mesogen Melting Point, °C		Aromatic Solvating Solvent Boiling Range, °C	Aromatic Carbon, %	Added Conc, %	Solvated Mesophase % Anisotropy	T@1000 P&100s^{-1}, °C
383	With	340-400	~82	17	100	294
		455-490	~84	17	100	305

Example 5.

[0041] Example 5 shows use of the inventive aromatic solvents as components of extraction solvents to isolate mesogens from mesogen-containing pitches. The extractions show excellent control of residue mesogen melting point by making small adjustments in the amount of aromatic solvent used.

Extraction Solvent		Solvated Meso. Residue	Dry Mesogen
Composition	Est. Sol. Param.	% Anisotropy	Melting Point, °C
Xylene	8.75	100%	390
95/5 Xylene/Aromatic Solvent	8.79	100%	409
90/10 Xylene/Aromatic Solvent	8.83	100%	429

Example 6.

[0042] Example 6 shows that aromatic solvents of the invention offer an economical option for obtaining high melting mesogens by extraction. The inventive solvents are inexpensive process byproducts that are effective in small amounts for controlling the melting point of mesogens obtained by extraction of mesogen-containing pitches.

Extraction Solvent		Solvated Mesophase Residue		Dry Mesogen
Composition	Est. Sol. Param.	% Anisotropy	T@1000 P&100s^{-1}, °C	Melting Point, °C
60/40 Xylene/Tetralin	8.78	100%	221	421
90/10 Xylene/Aromatic Solvent	8.83	99%	217	417

Example 7.

[0043] Example 7 illustrates the ability to spin smaller diameter pitch fibers from the relatively high boiling solvents of the invention. Each pitch was spun at a variety of temperatures and pitch flow rates to identify conditions giving the smallest green fiber diameter. Both inventive solvents are effective in allowing the draw of the solvated mesophase pitches of the examples to small diameter fibers. One skilled in the art of spinning mesophase pitch fibers will note that carbonized fibers from both exemplary green fibers will have <10μ average diameters.

Mesogen Melting Point, °C		Aromatic Solvating Solvent		Spinning	Green Fiber Ave. Min.
		Boiling Range, °C	Added Conc., %	Temp., °C	Dia., microns
383	With	340-400	17	328	12.4
		455-490	17	350	10.0

[0044] Whereas, the present invention has been described in relation to the drawings attached hereto, it should be understood that other and further modifications, apart from those shown or suggested herein, may be made within the spirit and scope of this invention.